CHAPTER 7

MEMBRANE TECHNIQUES

7-1. Electrodialysis. The ions in a water solution can be made to migrate by applying an electric field to the solution. By arranging various barriers to the flow of ions, it is possible to directly desalinate water with electricity. Such barriers are called ion-exchange membranes. Membranes that allow a reasonable flow of cations, but block or reduce the flow of anions, are called cationic-exchange membranes. Membranes that allow a reasonable flow of anions, but block or reduce the flow of cations, are called anion-exchange membranes. Membranes that pass both anions and cations are called neutral membranes.

a. Theory. In solutions containing dissolved ions, electric currents are carried by movement of the ions. Positive ions migrate in the direction of the current flow, and negative ions migrate against the current direction. When the anions are blocked by a cationic-exchange membrane, they stop and form a localized charge at the membrane face. This accumulated negative charge is neutralized by the flow of cations across the cationic membrane. This generates a concentrated solution on the side of a cationic-exchange membrane that faces the negative electrode. It also generates a dilute solution on the side of the cationic membrane that faces the positive electrode as shown in figure 7-1.

b. Electrodialysis stack. If both a cationic and anionic membrane are placed across a current flow in an electrolyte solution, the side of the cationic membrane facing the positive electrode and the side of the anionic membrane facing the negative electrode will become less saline. If the cationic membrane is closer to the negative electrode and the anionic membrane is closer to the positive electrode, the solution between the membranes will become less saline as the ions migrate in their respective directions. Any number of pairs of cationic and anionic membranes can be placed across a current-carrying solution, such that the cationic membrane is closest to the negative electrode, and the solution between will be diluted (fig. 7-1). A battery of several such membrane pairs is called an electrodialysis stack. Several variations of the standard electrodialysis stack have been developed, but none have been proven superior to this standard stack of alternating cationic- and anionic-exchange membranes to desalinate natural brackish water.

c. Electrodialysis reversal. One important improvement now used in electrodialysis installations is to reverse the polarity periodically and move the ions in the opposite direction. This returns anions across the anionic membranes and helps break up scale formed on the concentrating face of the membranes. Water will flow osmotically across both membranes from the dilute product stream to the concentrated brine stream in an electrodialysis-reversal stack. This osmotic product water loss concentrates uncharged material, such as turbidity and bacteria. This concentration effect must be considered during the design to ensure meeting water turbidity and product water bacterial count requirements. Most electrodialysis membranes are not tolerant of chlorine. When possible, water desalinated by electrodialysis reversal should be disinfected after desalination is completed. The membranes should be protected by a 10-micron cartridge filter.

7-2. Electrodialysis-reversal design. When electrodialysis reversal can be shown to be the most economical process for desalination, then only an electrodialysis-reversal system will be designed. When the process selection does not yield a specific process, then designs must be prepared for more than one process.

a. Identification of work. The design engineer will be made aware of the base site and construction schedule. The location and time schedule will be considered in the design; this includes the date the system must be online. The minimum number and minimum capacity of the modules will be determined. Any restrictions that storage will place on maximum allowable downtime will also be considered. A maximum allowable output conductivity in the product water will be determined, based on the worst possible feed water.

b. Existing on planned facilities. When electrodialysis reversal is being designed, it is essential to determine the types of available electrical power. The voltage, phase, frequency, and available amperage of all electrical power sources, planned or existing, must be considered in the design.

c. Raw water information. One of two circumstances will limit the quantity of raw water consumed. Both of these limitations must be considered in the design:

-The availability of raw water may place a limitation on the raw water used in the process.
-The maximum amount of waste brine that can be economically disposed of may limit the raw water used in the process.

The principle requirement in a desalination design is an accurate projection of the chemical makeup of the worst quality water that will ever be used as a raw feed water at the site being investigated. The design documentation must include maximum total dissolved solids, the individual ions (see App. B), the maximum amount of total suspended solids present in the feed water, and any gas or potential corrosive agent that may be in the feed water.

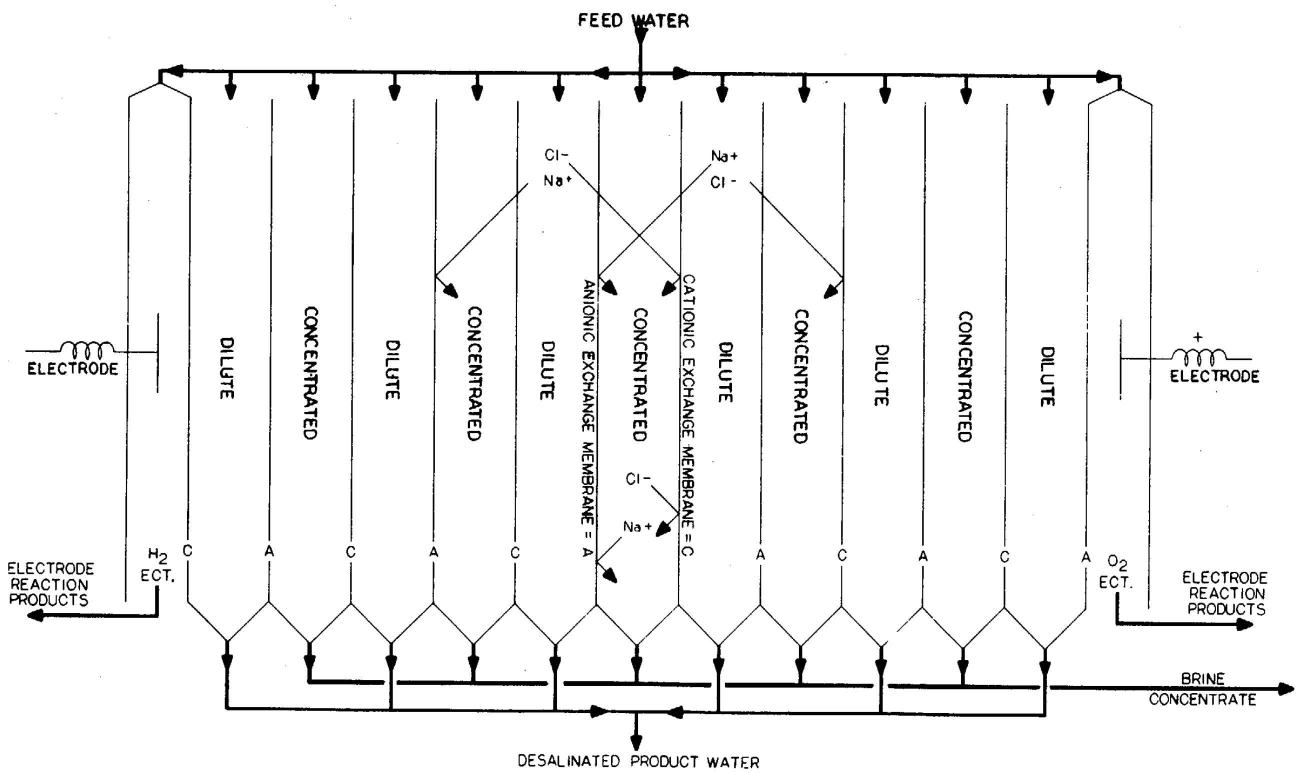

Figure 7-1. Principles of electrodialysis desalination

d. Process specifications. When an electrodialysis-reversal process has been identified as most economical, the design will be limited to the single process. The process design for any electrodialysis-reversal process will include a minimum/maximum allowed product water conductivity. The design must show the required product conductivity that must be obtainable at the required product flow, based on the worst conductivity raw water. A 10-micron cartridge filter to be placed before the membranes must be included in the design. When a particular metallurgy or material is required for strategic, corrosion design, or process economic reasons, this metallurgy or material will be designated for all applicable parts and spare parts and equipment. All required instrumentation, including a voltmeter and an ammeter, for each electrodialysis-reversal stack must be designed. The system design must be based on equipment with a history of water treatment system experience. The required experience history should include a minimum of 2 years of operating experience meeting water quality and system design goals, current operating capacity, maximum allowable repair frequency and duration, and maximum allowable ratio of experienced capital cost to repair cost. The requirement for successful experience will limit the amount of untested innovation used at a facility.

7-3. Reverse osmosis. Diffusion through materials is influenced by the nature of the diffusing material. A number of materials allow water to pass through with relative ease. Some of these materials allow only a minute passage of ionized material compared to the passage of water through them. These semipermeable materials are used for desalination. If a thin barrier or membrane is used, water can be forced through the membrane while ions are stopped by the membrane. In general, nonionized materials, such as some gases and many organics, will not be removed by these membranes. Some larger organic molecules may not pass through the membranes.

a. Osmotic pressure. When a semipermeable membrane that will pass solvent is placed between two solutions of different concentrations containing the same solvent at identical temperatures, the solvent must pass from the less concentrated to the more concentrated solution as shown in figure 7-2. This flow of solvent produces a pressure head difference. The equilibrium liquid pressure head difference is called the osmotic pressure difference of the solutions (see App A for the calculation). If these pressures are reversed, pure water will be forced from the more concentrated solution through the membrane into the less concentrated solution, provided that the pressure differential exceeds the osmotic pressure. A typical reverse osmosis flow sheet is shown in figure 7-3.

b. Energy recovery. Reverse osmosis produces a concentrated, high-pressure brine. With reverse osmosis, the energy lost in depressurizing the brine can be returned efficiently to the feed water by mechanical methods. In small systems, consider a flow-work exchanger; in large systems, consider an energy recovery turbine.

(1) *Flow-work exchanger*. A flow-work exchanger, figure 7-4, is a simple piston driven by pressurized brine to compress the saline feed. When the piston has traveled a full stroke, the valving is changed, and the saline feed is used to expel depressurized brine. Flow-work exchangers have been under development since 1980.

(2) *Energy recovery turbines*. Several large reverse osmosis systems have been built with energy recovery turbines. These turbines can be installed to assist directly in pumping or to drive synchronous motors and generate electricity. While reverse osmosis is an energy efficient desalination process for highly saline waters, energy recovery can reduce the amount of energy used by as much as one-third.

c. Mechanical strength and packing of membranes. For containment of high pressures with thin membranes in reverse osmosis, three alternative arrangements have been developed.

(1) *Porous tubes*. Porous tubes lined with semipermeable membrane material have been developed for concentration of valuable products in industry. Such systems are no longer used for water desalination. A packing density of less than 110 square feet of surface area per cubic foot of volume makes this configuration too expensive for water production. See figure 7-5.

(2) *Spiral-wound membranes*. By using spacers it is possible to roll a membrane envelope onto a slotted product water tube as shown in figure 7-6. This reverse osmosis membrane configuration is known as the spiral-wound configuration. This arrangement allows for surface densities of greater than 250 square feet of surface area per cubic foot of volume. With the development of this spiral-wound configuration, water production from brackish water sources by reverse osmosis became economical in many applications. See figure 7-6.

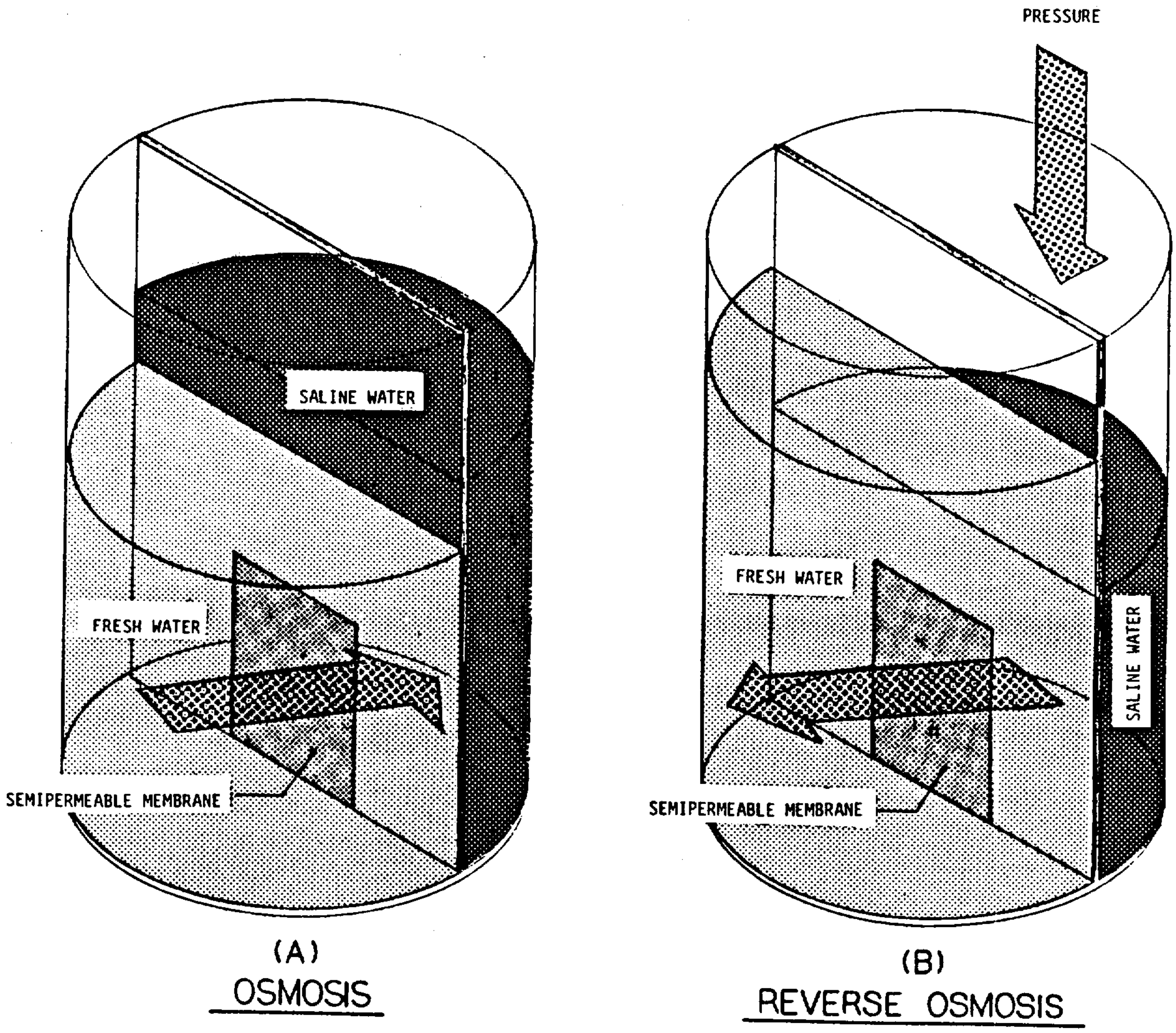

Figure 7-2. Revere osmosis principles.

(3) *Hollow fine fibers*. A large research and development effort made it possible to coat minute hollow fibers, smaller in diameter than a human hair, with semipermeable membrane material. This reverse osmosis membrane configuration is known as the hollow fine-fiber configuration. Packing densities with hollow fine fibers have exceeded 4,900 square feet of surface area per cubic foot of volume. See figure 7-7.

d. Membrane materials. There area number of successful reverse osmosis membrane materials. Currently, two principal types of membrane materials are being used: cellulose acetate and polyaromatic amide. Both materials are destroyed by dehydration of the membranes. To avoid dehydration, product water must be supplied to allow osmotic water to flow back through the membranes in order to dilute the feed water to approximate product water concentrations. If product water is not supplied, then the osmotic suction, if the feed water side of the membrane is depressurized, will draw air back into the membranes and dehydrate them. Usually, the required volume of product water is supplied by a suck-back tank, which maintains a minimum volume and back pressure on the reverse osmosis membranes.

(1) *Cellulose acetates*. This material suffers from slow chemical decomposition through a process called hydrolysis. The use of acids to prevent scaling increases the rate of this form of membrane decay. Cellulose acetates are also biodegradable and must be protected from bacterial attack. One of the important advantages of cellulose acetate is its resistance to attack by chlorine.

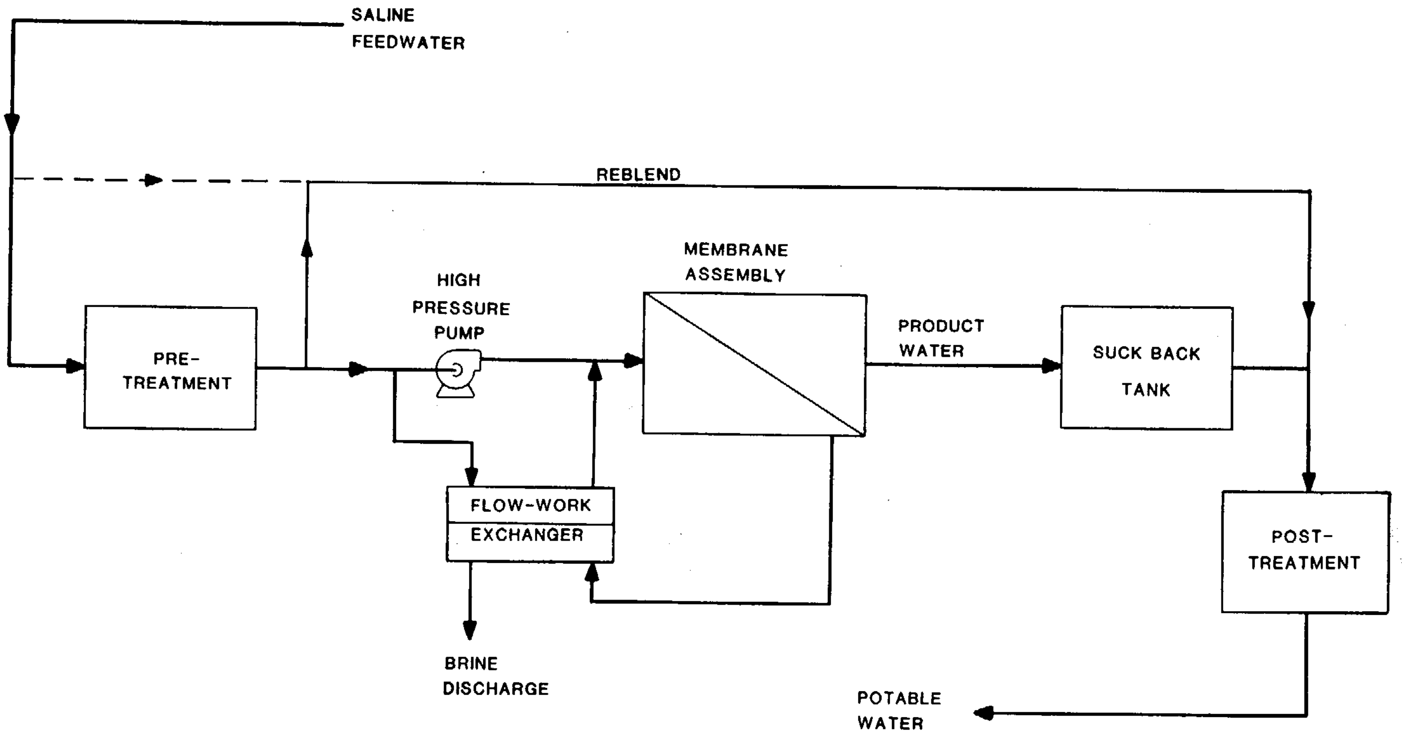

Figure 7-3. Reverse osmosis desalination system.

Most cellulose acetate membranes can be used with feed waters containing less than 1 milligram per liter of residual chlorine, which will protect the membranes from biological attack.

(2) *Polyaromatic amides*. These membranes are stable, biologically and chemically. Despite this chemical stability, these membranes cannot tolerate any residual oxidant. If chlorination is required to reduce the amount of biological suspended solids, then dechlorination must be complete if polyaromatic amide membranes are used.

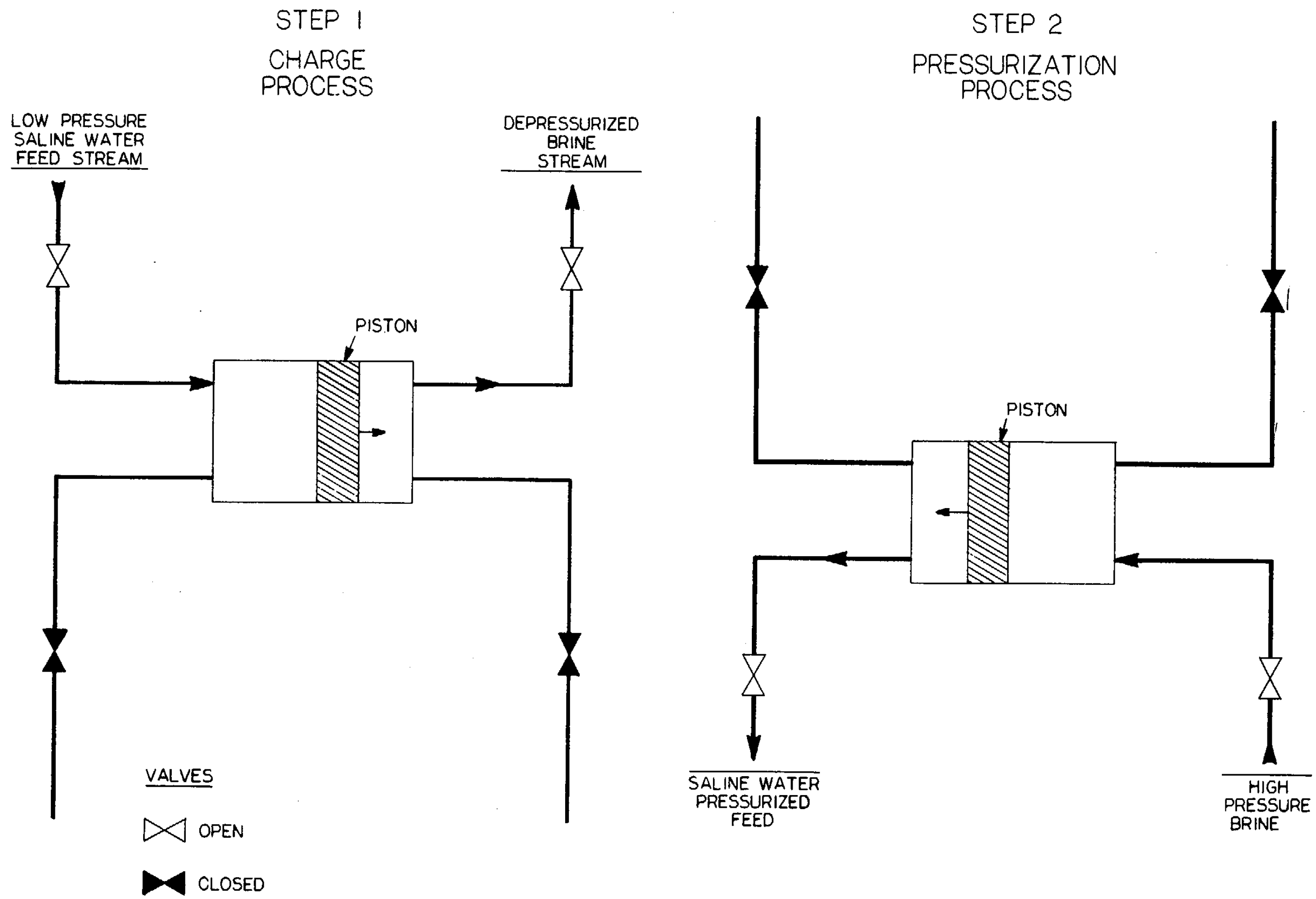

Figure 7-4. Flow-work exchanger principles.

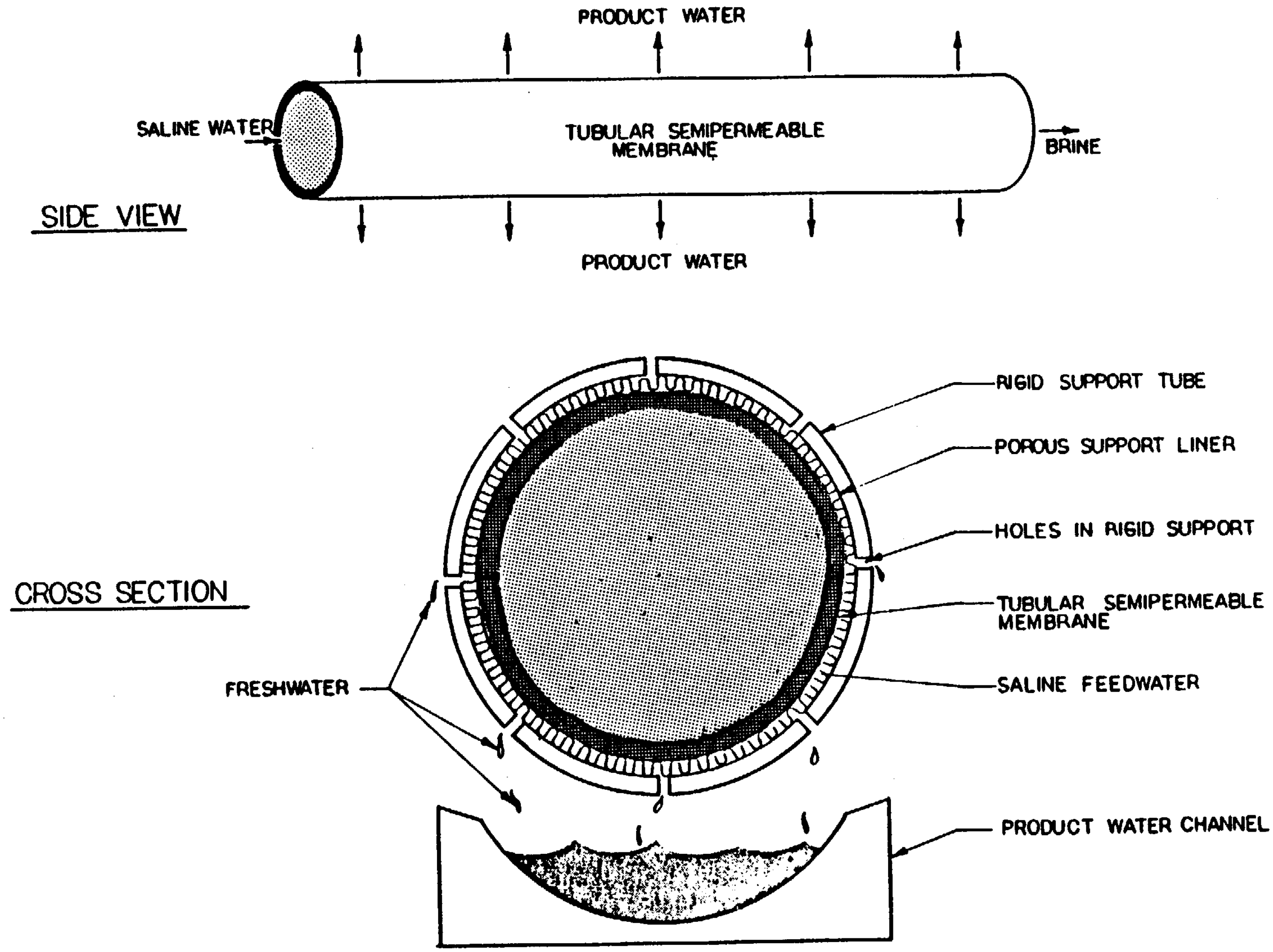

Figure 7-5. Construction of a tubular reverse osmosis membrane.

7-4. Reverse osmosis membrane staging configurations. Two kinds of membrane staging are commonly used in reverse osmosis desalination plants: product staging and reject staging. Reject staging is used to treat waters with low salinity, so that most of the raw feed water will eventually be recovered as product water. Product staging is used to treat highly saline waters, whose product water salinity cannot be reduced to the required concentration by a single pass through the membrane under consideration. Banking is the term usually used for parallel arrangement of a number of membrane modules operating from the discharge of a single pump.

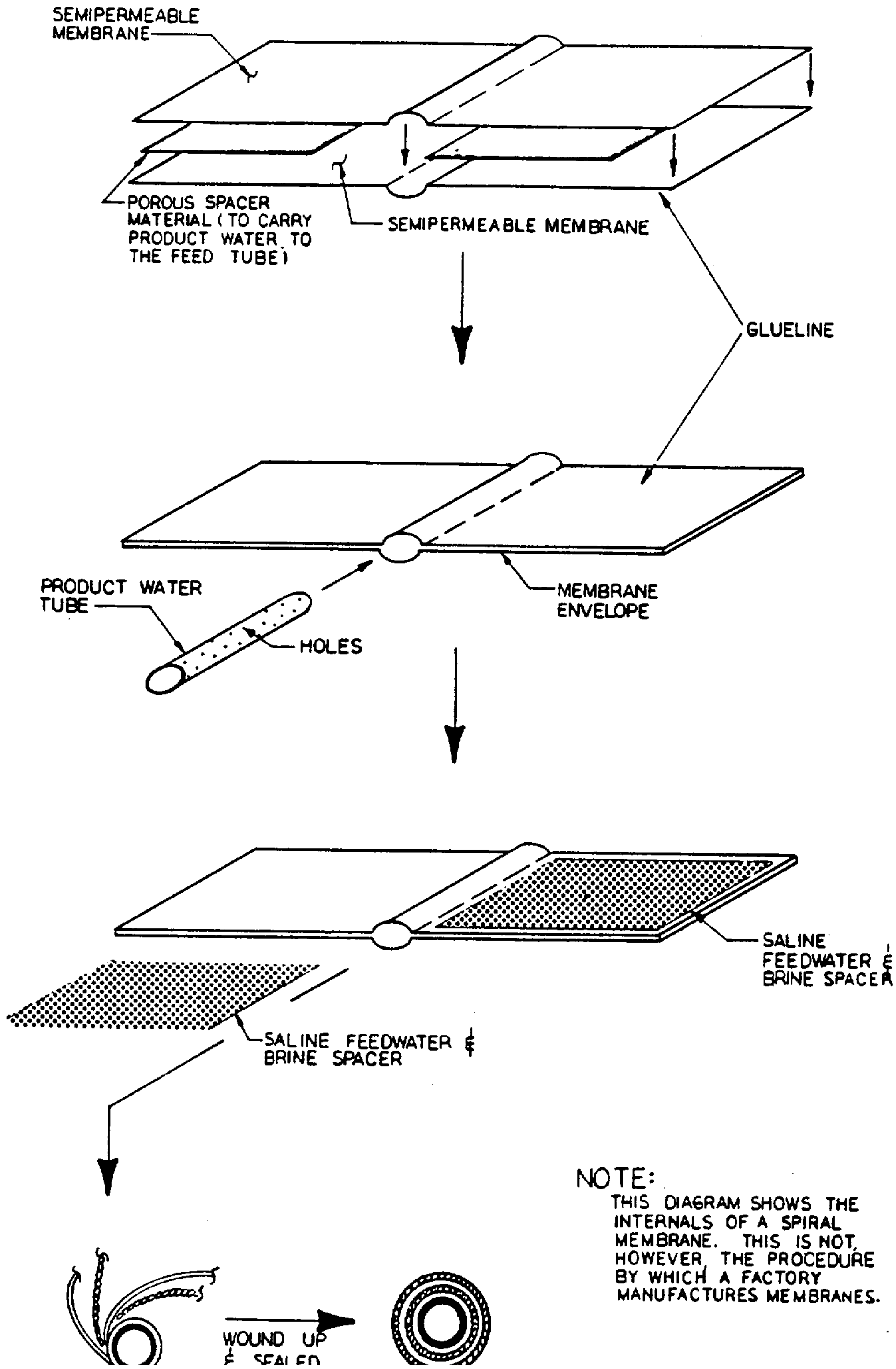

Figure 7-6. Internal construction of a spiral-wound membrane.

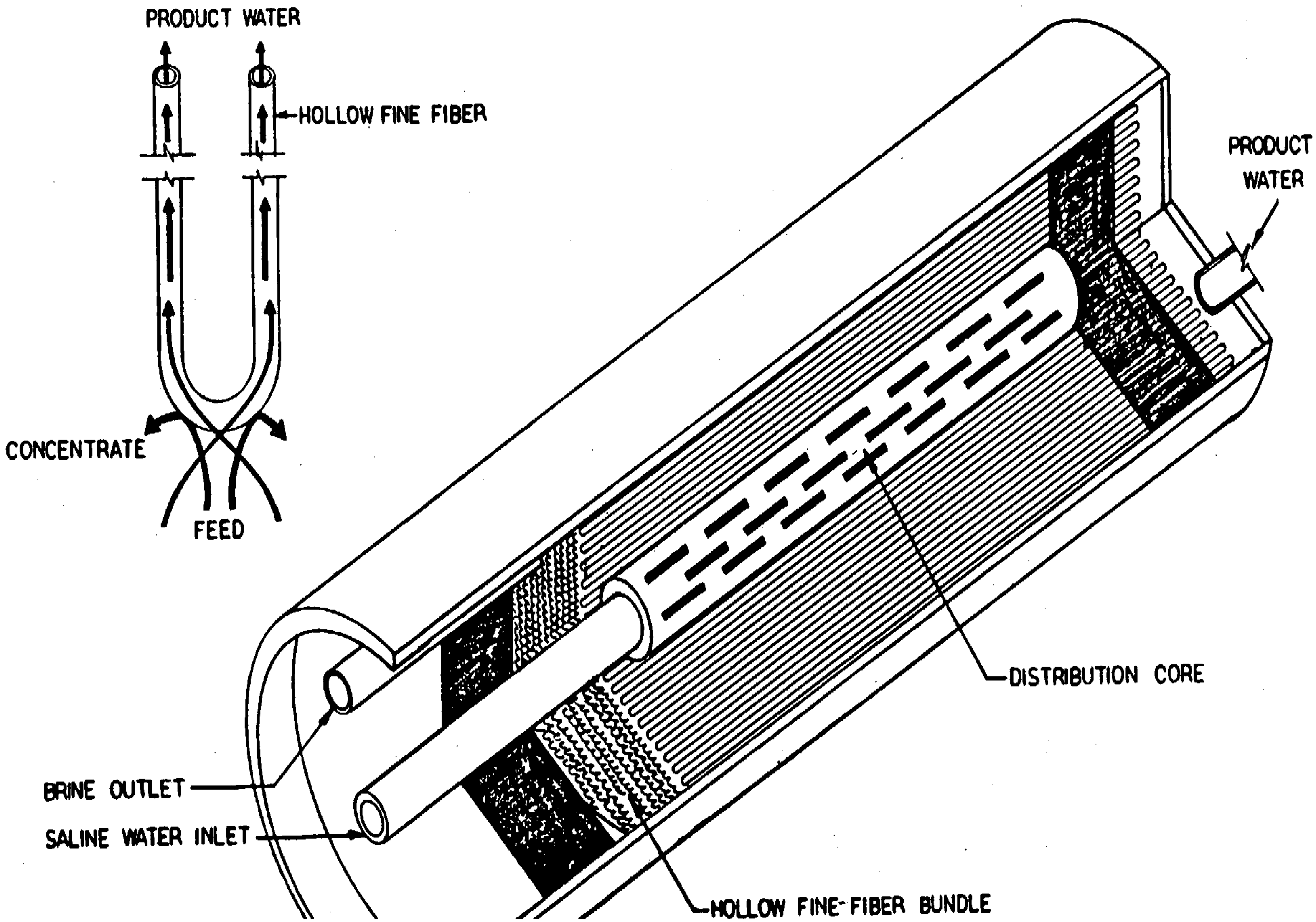

Figure 7-7. Internal construction of a hollow fine-fiber reverse osmosis membrane module.

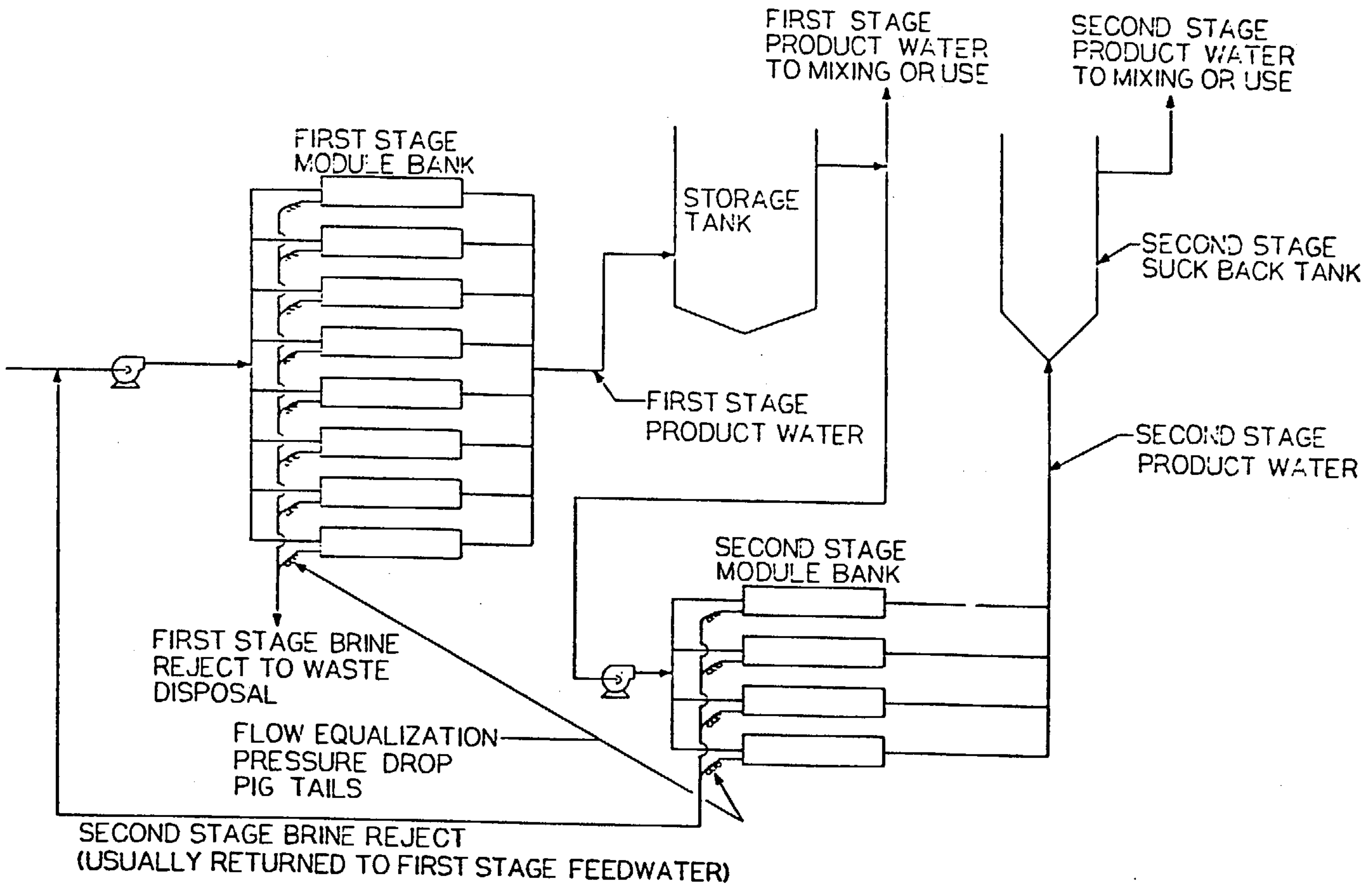

Figure 7-8. Reverse osmosis product staging.

Banking of membranes usually require a flow restraint on the brine reject of each module in the bank. A pigtail of nylon tubing is often used for this flow equalization headloss. This pressure drop maintains a balanced flow of brine out of each membrane module in the bank. Unbalanced flow can shorten the useful life of membrane modules. While higher flow rates will tend to clean membranes, excessive flow can fatigue or fray both spiral and hollow fine-fiber membranes. Low flow rates allow the concentrated brine to stagnate, which leads to scaling and fouling of membrane surfaces.

a. Product staging. Product staging is true series operation of two or more reverse osmosis membrane systems, as shown in figure 7-8. Product staging is used when a single pass through one reverse osmosis membrane does not bring a constituent concentration down to specification. The second stage always requires its own pressurizing pump, taking suction from the suck-back or storage tank of the first stage reverse osmosis system. When the water produced from the second stage is significantly lower in dissolved constituents than required, the product water from the first stage may be blended with the second stage product to produce the desired water quality. When potable water and other waters with lower dissolved solids content are required, a product staging system can be used to supply the desired quality or qualities between that of the first and second stage product. Life cycle costing should be used to evaluate dual- and triple-distribution systems where product staging is required.

b. Reject staging. Reject staging, figure 7-9, is used when the low salinity of the raw water permits a high water-recovery ratio. Most membrane module manufacturers have a minimum allowable brine reject flow for any given membrane of their manufacture. The manufacturer's recommended maximum feed water flow rate and minimum recommended brine reject flow can be used to calculate a maximum recommended single stage recovery fraction by use of the following equation:

$$\frac{F - B}{F} = R$$

Where:

F = Maximum recommended feed flow per module

B = Minimum recommended brine reject flow per module

R = Maximum recommended recovery rate

This maximum single stage water recovery is one means of evaluating a membrane module being considered for low salinity reverse osmosis desalination. When the reject stream is still diluted enough for further concentration after the maximum recommended recovery ratio is reached, the brine can be piped directly into another membrane module for further water recovery. This is accomplished by combining the brine flow from a number of first stage modules onto a fewer number of secondary membrane modules. It is occasionally possible to further concentrate the brine on a third reject stage as shown in figure 7-9. The design of reject staging, in order to balance the utilization of the membrane modules for optimum economical life cycle cost, is a complex activity to be performed by the membrane manufacturer or Operations Engineering Manufacturer.

c. Combined product and reject staging. In the desalination of highly saline waters such as seawater, product and reject staging can be effectively combined. The second stage of a product staged system can be designed as a reject staged subsystem. Any of three factors may limit reverse osmosis water recovery: osmotic pressure; sparingly soluble salts; or turbidity. Water from a primary reverse osmosis treatment system will have three properties pertaining to these limitations:

-A lower osmotic pressure than the raw feed water.

-A disaproportionately reduced concentration of divalent ions.

-No turbidity.

These qualities of primary reverse osmosis product water can allow for greater water recovery from a secondary product staged reverse osmosis subsystem than is allowed by the manufacturer's maximum recommended recovery rate. When the water recovery of the second stage of a product staged system can be increased by reject staging, the secondary stage shall be reject staged. When the brine from the secondary stage of a product staged system is less concentrated than the primary stage feed water by more than 1,000 milligrams of total dissolved solids per liter, the use of dedicated desalination of this lower concentration water shall be life cycle costed. This life cycle cost for dedicated secondary stage brine desalination shall be compared with the life cycle cost of blending the secondary stage brine into the primary stage feed water.

7-5. Reverse osmosis system design. When process selection does not yield a specific membrane or even a particular process, then designs must be prepared for more than one process.

a. Identification of work. When a schedule and a base site have been selected, this information will be made available to the design engineer. The identification of the location and the time schedule will be considered in the design; this includes the date the system must be online. The minimum number of independently operable membrane banks and the minimum capacity of the banks must be determined. Any restrictions that storage will place on maximum allowable downtime will also be determined.

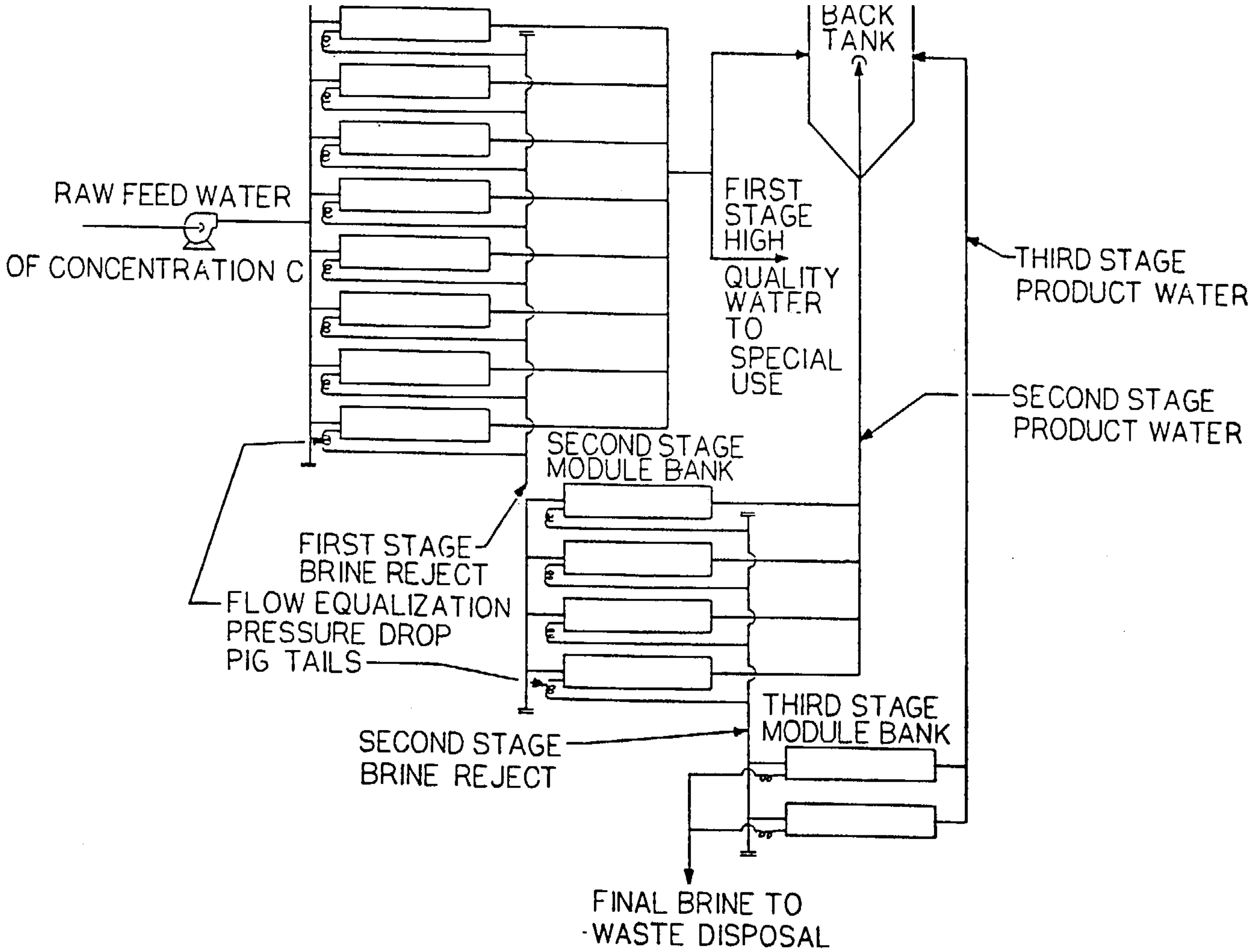

Figure 7-9. Reverse osmosis membrane reject staging.

All reverse osmosis designs will consider a minimum membrane rejection for all objectionable materials in the pretreated saline water.

b. Existing or planned facilities. Reverse osmosis design must include information on the available sources of mechanical energy. Electrical power is the most common energy source for conversion to mechanical pumping energy. The phase, voltage, frequency, and amperage of all available or planned electrical power will be determined. The process design, particularly with respect to pumping and pretreatment, must be detailed clearly.

c. Raw water information. As with other desalination systems, one of two limitations exist on the quantity of raw water to be desalinated.
Both of these limitations must be considered in the design:

- -The maximum amount of waste brine that can be economically disposed of may place a limitation on the raw water used in the process.
- -Availability of the raw water may limit the raw water used in the process.

The principle requirement in a reverse osmosis design is an accurate projection of the chemical, biological, and physical makeup of the poorest quality water that will ever be used as raw feed water at the site being investigated. The design documentation must include the following:

- -Maximum total dissolved solids.
- -Maximum concentration of every ion that could precipitate or influence the activity coefficient of a precipitation reaction. (See App. B.)
- -Maximum concentration of each ion that must be controlled in the product water.
- -Concentration of both molybdate reactive and molybdate nonreactive silica.
- -Maximum allowable concentration of nonionizable material.
- -An oil and grease analysis to levels below 10 milligrams per liter.
- -Any gas or potential corrosive agent that may be in the feed water.

d. Process design. When a particular membrane has been identified as the most economic, the design will be limited to the one membrane type. The process design for any reverse osmosis process will consider raw water quality and the required final product water quality. A suitable tank to meet suck-back requirements will be designed for all membranes that could be damaged by dehydration. The system design must be based on equipment with a history of successful water treatment experience. The required experience should include a minimum of 2 years of experience, treatment capacity, repair frequency and duration, and a ratio of repair cost to capital cost. The requirement for successful experience will limit the amount of untested innovation used at a facility. When a particular metallurgy or material is required for strategic, corrosion design, or process economic reasons, this metallurgy will be included for all applicable parts and spare parts and equipment.

7-6. Materials of construction.

Ferric ions will cause severe problems in membrane systems. For this reason, never permit carbon steel to be in contact with the feed water being supplied to a membrane desalination plant. Use nylon or other plastics capable of maintaining the desired pressures whenever possible. Use 316L stainless steel for pump impellers and other feed-water-contact metal surfaces if hexametaphosphate is used for scale control. If no scale inhibition is necessary, use bronze for pump impellers.